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(54) Title of the invention      Resin composition for fixing hair colorant and hair colorant using the same

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*application*

*45-85%*

*10-30%*

*1-20%*

*1-30%*

*a*

*b*

*c*

*c*

*25, e*

*Mori*

*(a) maybe*

*(b) overlaps*

*(a) overlaps*

*(c) overlaps*

*features that contribute to hardness/softness 20-50%*

*5-25%*

*30-70%*

*5-20%*

## Specification

### 1. Title of the invention

Resin composition for fixing hair colorant and hair colorant using the same

### 2. Scope of the patent claims

(1) A resin composition for fixing hair colorant, obtained by copolymerizing polymerizable monomers a to d below then neutralizing water-soluble organic basic substance

- 10 a. from 30 to 70% by weight of at least one monomer from acrylate esters and/or methacrylate esters represented by the following formula



- 15 (in the formula,  $R_1$  is a hydrogen atom or methyl group,  $R_2$  is a methyl group or ethyl group, and  $n$  is an integer from 1 to 10)

- b. from 5 to 25% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid
- c. from 5 to 20% by weight of at least one monomer from C8-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid
- 20 d. from 20 to 50% by weight of other vinyl-based monomer.

(2) A hair colorant containing the resin composition for fixing hair colorant as claimed in claim 1.

### 25 3. Detailed description of the invention

#### Field of industrial use

The present invention relates to a resin composition for fixing hair colorant, specifically a resin composition which fixes hair colorant such as the pigments and the like used to temporarily color hair, and to a hair colorant which uses the same.

#### 30 Prior art

Colorants for hair cosmetics such as color foams, color sprays, mascara-type agents and colorants for gray hair obtained by mixing hair colorant and resin for the fixing thereof are known agents for the temporary coloring of hair. Mascara-type agents, color sprays and color foams use ethanol, water or the like as solvent, and the color spray or color foam is loaded into a pressure-resistant aerosol vessel together with a propellant such as fluorocarbon gas.

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Known examples of the abovementioned resins used for fixing hair colorants include vinylpyrrolidone-vinyl acetate copolymers, copolymers comprising methacrylate ester and monochloroacetate-modified N,N'-dimethylaminoethyl-methacrylate, and acrylate ester-methacrylate ester copolymers.

However, the abovementioned vinylpyrrolidone-vinyl acetate copolymer is disadvantageous in that, for example, the resulting film is hard before it absorbs moisture, and when it does absorb moisture it quickly softens and becomes sticky. Copolymers of methacrylate esters and monochloroacetate-modified N,N'-dimethylaminoethyl methacrylate are also disadvantageous in that, for example, they are highly hygroscopic and there is considerable color loss when wet. Acrylate ester-methacrylate ester copolymers are also disadvantageous in that, for example, in the case of common setting agents, the resulting film is hard, flaking prevention is inadequate, there is no soft feel and hair washability is poor.

Problems to be overcome by the invention

Accordingly, an object of the present invention is the provision of a resin composition for fixing hair colorant, and a hair colorant using the same, which offers good hair washability, has good adhesion to hair, results in the formation of a soft film, is water resistant and does not result in color loss when rubbed.

Technical means for overcoming the problems, and use thereof

The inventive resin composition for fixing hair colorant is obtained by copolymerizing the following polymerizable monomers a to d then neutralizing using a water-soluble organic basic substance

a. from 30 to 70% by weight of at least one monomer from acrylate esters and/or methacrylate esters represented by the following formula



(in the formula, R<sub>1</sub> is a hydrogen atom or methyl group, R<sub>2</sub> is a methyl group or ethyl group, and n is an integer from 1 to 10)

b. from 5 to 25% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid

c. from 5 to 20% by weight of at least one monomer from C8-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid.

d. from 20 to 50% by weight of other vinyl-based monomer;

moreover, the inventive hair colorant contains the abovementioned resin composition for fixing hair colorant, and hair colorant or the like.

The abovementioned monomer a improves the luster and the adhesiveness of the resin with respect to hair, and it controls hydrophilicity, hair washability and the like; the amount used is from 30 to 70% by weight, preferably from 35 to 60% by weight, with respect to the total amount of polymerizable monomer. If the amount  
5 used is less than 30% by weight, there is poor adhesion to hair, poor luster and the like, and the hair washability deteriorates, whereas if more than 70% by weight is used, the system becomes too hydrophilic and water resistance decreases.

Specific examples of monomer a include methoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytetraethylene (meth)acrylate,  
10 methoxypolyethylene glycol #400 (meth)acrylate, ethoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, ethoxytetraethylene glycol (meth)acrylate, ethoxypolyethylene glycol #400 (meth)acrylate and the like, and these acrylate esters and methacrylate esters can be used individually or combinations thereof can be used.

15 Monomer b also contributes to the hair washability and hydrophilicity of the resin, and the amount used is from 5 to 25% by weight, preferably from 10 to 25% by weight. If less than 5% by weight is used, the resulting film becomes sparingly soluble in water and so the hair washability will be poor, whereas if more than 25% by weight is used, moisture absorption increases and stickiness becomes marked.  
20 As described above, unsaturated carboxylic acids chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid can be used, either individually or in combination, as monomer b.

Monomer c contributes to the water resistance and softness of the resulting film, and the amount used is from 5 to 20% by weight, preferably from 5 to 15% by  
25 weight. If less than 5% by weight is used, the film is hard and the water resistance is poor, whereas if more than 20% by weight is used, the film becomes too soft, stickiness is marked and hair washability deteriorates.

Specific examples of monomer c include 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate and the like, and these  
30 acrylate esters and methacrylate esters can be used individually or in combination.

Monomer d contributes to the appropriate hardness and softness and the like of the resulting film, and the amount used is from 20 to 50% by weight.

Specific examples of monomer d include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl  
35 (meth)acrylate, vinylacetate, vinyl pyrrolidone, (meth)acrylamide, diacetone (meth)acrylamide, acrylonitrile, styrene and the like, and these vinyl-based monomers can be used individually or in combination.

The copolymerization of the abovementioned monomers a to d can be performed according to common solution polymerization in a hydrophilic solvent, for example, it can be performed by dissolving the monomers in hydrophilic solvent, adding polymerization initiator then agitating under a current of nitrogen at the boiling point of the solvent or a temperature close thereto. The copolymerization can proceed in the presence of the total amount of all types of abovementioned monomer from the start of the polymerization, or different types and/or amounts of monomer can be added in portions. The abovementioned solvent is preferably used such that the solids content in the resin solution is from 30 to 60% by weight.

Examples of hydrophilic solvents include C1-4 aliphatic alcohols which can dissolve in water such as methyl alcohol, ethyl alcohol, isopropyl alcohol and butyl alcohol; alcohols which contain water such as 95% ethyl alcohol; and acetone, methyl cellosolve, ethyl cellosolve, dioxane, methyl acetate, dimethylformamide and the like, and these can be used individually or in combination. It is preferable to use a peroxide such as benzyl peroxide or lauryl peroxide, or an azo-based compound such as azobisisobutyronitrile, or the like as the polymerization initiator.

By adding water-soluble organic basic substance to the resin-containing solution obtained as a result of the abovementioned copolymerization, the copolymerized resin is both neutralized and rendered water-soluble. The degree of neutralization is preferably from 50 to 100%.

Specific examples of water-soluble organic basic substances which can be used include ammonia water, mono-, di- or triethanolamine, mono-, di- or triisopropanolamine, morpholine, aminomethylpropanolamine, aminoethylpropanolamine, aminomethylpropanediol, aminoethylpropanediol and the like, and these can be used individually or in combination. When an organic amine is used, the resulting resin composition does not contain water, and this is particularly preferable in aerosols which repel water.

The resulting resin composition is such that the molecular weight of the copolymer is from around 5 000 to 200 000, and the hydrophilic solvent solution obtained as a result of the abovementioned copolymerization can either be used without further modification, or as a water-containing solvent system, in order to fix hair colorant, preferably at a (hair colorant/resin composition) ratio (solids ratio) of from (1/1) to (1/20).

Working examples 1 to 6

The present invention is described below based on working examples. It should be noted that "parts" and "percent" are based on weight.

Production of the resin composition

200 parts of polymerizable monomer a to d, 100 parts of ethanol and from 0.5 to 2 parts of polymerization initiator were introduced into a 1 l four-necked flask provided with a reflux condenser, thermometer, glass tube for nitrogen substitution, dropping funnel and agitator, and the system was heated under reflux at 80°C under a current of nitrogen for 4 hours to allow polymerization to proceed. After the polymerization, the system was cooled, an ethanolic solution of water-soluble organic basic substance was added at 50°C, and the system was diluted using ethanol to a solids content of 50%.

Table 1 shows the polymerizable monomer a to d compositions, and the types and amounts of polymerization initiator and water-soluble organic basic substances used in working examples 1 to 6 and comparative examples 1 to 6.

Table 1 Monomer composition (parts), degree of neutralization (%) and average molecular weight (x1 000) of the resin

		Working example						Comparative example					
		1	2	3	4	5	6	1	2	3	4	5	6
Part		part	part	part	part	part	part	part	part	Part	part	part	part
Monomer a	Methoxytetraethylene glycol methacrylate	70						30					
	Ethoxydiethylene glycol acrylate		120						160				
	Methoxypolyethylene glycol #400 methacrylate			80						70			
	Methoxydiethylene glycol methacrylate				110						110		
	Ethoxytetraethylene glycol acrylate					100	100					100	100
Monomer b	Methacrylic acid	40	10	40		40	30	40	5	60		40	30
	Acrylic acid			10	20					20	5		
	Itaconic acid		10						5				
Monomer c	Stearyl methacrylate	30						30					
	Dodecyl methacrylate		20		20				5		40		

	2-ethylhexyl methacrylate			30							20			
Monomer	Stearyl acrylate					20		30				5		60
	Methyl methacrylate			40				40			30			10
	Ethyl methacrylate	50				40			100			55		
	Butyl methacrylate		40		50					25		45		
Polymerization initiator	Azobisisobutyronitrile	1			1				1			1		
	Benzyl peroxide			2							2			
	Lauryl peroxide		2			1		2		2		1		2
	Monoethanolamine	19.9							19.9					
Organic basic substance	Triethanolamine				33.1			41.6				10.4		41.6
	Ammonia water (25% aqueous solution)			41.0							59.7			
	Morpholine		21.2			28.3				10.6		28.3		
	Degree of polymerization of the resin (%)	70	90	90	80	70		80	70	90	90	100	70	80
Average molecular weight of the resin (x1 000)		70	80	100	80	70		65	65	100	120	75	80	60



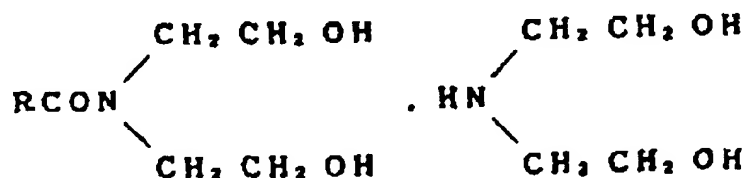
### Color base preparation

40% of the abovementioned resin composition of the comparative examples and working examples (solids content 50%) was mixed with 10% carbon black, as hair colorant, and 50% ethanol, and the color base was prepared using a three-stage roller.

### Color foam preparation

Colorants for hair comprising the three types of color foam compositions described below (type A: fast defoaming; type B: defoaming intermediate between type A and type C; type C: slow defoaming) using the abovementioned color base.

Composition (%)	Type A	type B	type C
Color base	10	10	10
Pullulonic-based nonnionic activator *1	-	0.5	-
Fatty acid diethanolamide *2	-	-	1
Cetyl alcohol	-	-	0.1
Ethanol	60	59.4	58.9
Purified water	20	20	20
LPG (liquefied petroleum gas)	2	2	2
Fluorocarbon gas F-12	8	8	8
*1 Poloxyethylene-polyoxypropylene block copolymer oxypropylene glycol average molecular weight 1 750, ethylene oxide content in the whole molecule 80%			
*2 Coconut oil fatty acid diethanolamide 1:2 type			



### Color spray preparation

Hair colorants were prepared from the color sprays having the compositions described below, using the abovementioned color base.

#### Composition (%)

Color base	6
Ethanol	34
Fluorocarbon gas F-11	24
Fluorocarbon gas F-12	36

(In working example 3 and comparative example 3, ammonia water was used as the organic basic substance and so it was not possible to prepare a color spray)

#### Mascara-type preparation

5 Hair colorants were prepared comprising mascara types of the following composition, using the abovementioned color base.

#### Composition (%)

	Color base	10
	Resin composition (solids content 50%)	4
	Ethanol	10
10	Purified water	76

#### Performance appraisal

15 An appropriate amount of the abovementioned hair colorant was applied to 10 cm decolored hair samples of approximately 1 g, the samples were dried using a drier (warm air) then the hair was appraised as described below, and the results are shown in Table 2.

#### (1) Stickiness

The stickiness of the hair after drying was appraised by touch to the fingers

- 20 O: Not sticky  
Δ: Slightly sticky  
x: Very sticky

#### (2) Flaking

Whether or not the resin fell off when the hair was combed after drying was appraised

- 25 O: No fall-off  
Δ: Slight fall-off  
x: Considerable fall-off

Table 2 Performance appraisal

		Working example						Comparative example					
		1	2	3	4	5	6	1	2	3	4	5	6
Color	Type A	Part	Part	part	part	part	part	part	part	part	part	part	part
		O	O	O	O	O	O	O	Δ	Δ	Δ	O	Δ
		O	O	O	O	O	O	Δ	O	Δ	O	Δ	O
		O	O	O	O	O	O	x	Δ	O	x	O	x
		O	O	O	O	O	O	O	x	Δ	O	x	O
foam	Type B	1	1	1	1	1	1	2	2	3	3	3	2
		O	O	O	O	O	O	O	Δ	Δ	Δ	O~Δ	Δ
		O	O	O	O	O	O	Δ	O	Δ	O	Δ	O
		O	O	O	O	O	O	x	Δ	O	x	O	x
		O	O	O	O	O	O	O	x	Δ	O	x	O
	Type C	1	1	1	1	1	1	2	2~3	3	3	3	2
		O	O	O	O	O	O	O~Δ	Δ~x	Δ~x	Δ	Δ	Δ
		O	O	O	O	O	O	O~Δ	O	O~Δ	O	Δ~x	O
		O	O	O	O	O	O	Δ~x	Δ	O	x	O	Δ~x
		O	O	O	O	O	O	O~Δ	Δ~x	Δ	O	x	O~Δ

Color Spray	Stickiness	O	O	-	O	O	O	O	Δ	-	Δ	O	Δ
	Flaking	O	O	-	O	O	O	Δ	O	-	O	Δ	O
	Washability	O	O	-	O	O	O	x	Δ	-	x	O	x
	Water resistance	O	O	-	O	O	O	O	x	-	O	x	O
	Wear resistance	1	1	-	1	1	1	2	2	-	2	2	2
Mascara Type	Stickiness	O	O	O	O	O	O	O	Δ	Δ	Δ	O	Δ
	Flaking	O	O	O	O	O	O	Δ	O	Δ	O	Δ	O
	Washability	O	O	O	O	O	O	x	Δ	O	x	O	x
	Water resistance	O	O	O	O	O	O	O	x	Δ	O	x	O
	Wear resistance	1	1	1	1	1	1	3	3	3	3	3	3

(3) Washability

A 1% aqueous solution of commercial shampoo was prepared, and hair which had already been dried was washed at 35°C, then rinsed using water and dried, then the extent of fall-off was appraised.

- 5 O: No residue  
Δ: Small amount of residue  
x: Large amount of residue

(4) Water resistance

- 10 Hair which had been dried was immersed in water at 40°C for 30 s then removed, dried by hand using a white cloth, and the deposition of color onto the white cloth was appraised.

- O: No color deposition  
Δ: Slight color deposition  
15 x: Considerable color deposition (part dissolved)

(5) Wear resistance

- 20 An abrasion fastness meter (JIS P-8136) was used: white cotton cloth was fixed to a table and hair that had been dried was fixed above, and abraded 30 times using a 300 g load. The degree of color loss onto the white cloth was appraised from 1 to 5

- 1: Almost no coloration  
5: Coloration of the whole surface

25 Advantages of the invention

As described above, the present invention provides a resin composition for fixing hair colorant which has excellent adhesion to hair, results in a soft film, with no stickiness or flaking, and results in excellent washability, water resistance and abrasion resistance, and provides the hair colorant obtained using the same.

30

Patent applicant  
Agent

Goo Kagaku Kogyo K.K.  
Patent attorney J. Ando

Procedural Amendment Form (Voluntary)

May 22, 1989

5 Director General of the Patent Office B. Yoshida

1. Indication of the case

Patent application number 040245 of 1988

2. Title of the invention

10 Resin composition for fixing hair colorant and hair colorant using the same

3. Person making the amendment

Relation to the case Patent applicant

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5. Date amendment was ordered (voluntary)

20 6. Subject of the amendment The "Scope of the patent claims" and  
"Detailed description of the invention" sections of the Specification

7. Details of the amendment See attached sheet

25 (Attached sheet)

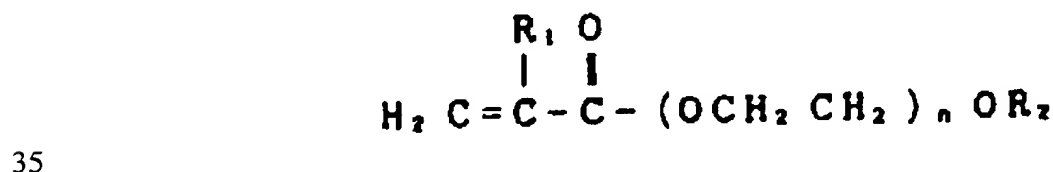
Details of the amendment

(1) The scope of the patent claims is amended as indicated on the attached sheet.

(2) In the specification,



is amended to



(3) In the specification,      ethanol                      60      59.4      58.9  
   purified water              20      20      20

is replaced with

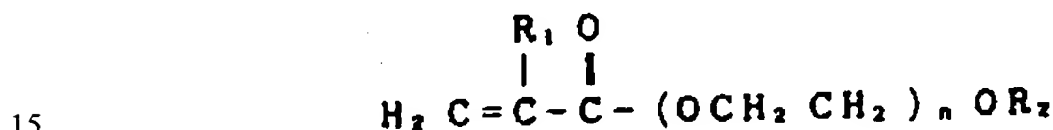
5     ethanol                      20      20      20  
   purified water              60      59.4      58.9

(attached sheet)

Amended scope of the patent claims

10 (1) A resin composition for fixing hair colorant, obtained by copolymerizing  
polymerizable monomers a to d below then neutralizing water-soluble organic basic  
substance

a. from 30 to 70% by weight of at least one monomer from acrylate esters  
and/or methacrylate esters represented by the following formula



(in the formula, R<sub>1</sub> is a hydrogen atom or methyl group, R<sub>2</sub> is a methyl group or ethyl  
group, and n is an integer from 1 to 10)

20 b. from 5 to 25% by weight of at least one monomer chosen from the group  
consisting of acrylic acid, methacrylic acid and itaconic acid

c. from 5 to 20% by weight of at least one monomer from C8-18 aliphatic alcohol  
esters of acrylic acid and/or methacrylic acid

d. from 20 to 50% by weight of other vinyl-based monomer.

25 (3) A hair colorant containing the resin composition for fixing hair colorant as claimed  
in claim 1.

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